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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in or relating to the Stabilization of Edible and Potable Substances against Oxidation

I, JOHAN ERNST NYROP, a Subject of the King of Denmark, of Nr 43 Eggersvej, Hellerup, Denmark, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

The present invention relates to a method for the stabilizing against oxidation of edible or potable materials containing organic substances subject to deterioration by oxidation, especially the prevention of or suppression of oxidation processes which occur at a comparatively high redox potential. Said materials generally contain unsaturated carbon compounds such as oxidizable flavouring substances and particularly fatty substances, carotinoids, vitamins, coffee extract, chlorophyll, xanthophyll, lycopin, and hormones.

It is well known that a very great number of edible or potable materials containing constituents of the above kind are liable to undergo undesirable changes on storage due to oxidation processes taking place in the material. The various cases of such deleterious oxidative changes are too numerous to be enumerated but some very common and well known representative examples may be mentioned. Thus, fatty emulsions are liable to become rancid on lengthy storage, and they may assume a fishy or tallowy taste. If the attempt is made to concentrate or dehydrate a coffee extract by evaporation, it loses its flavour. Vegetable oils are liable to become rancid in the course of time. Butter is also deteriorated by storage, and the same applies, e.g., to bacon and fat-containing sausages and the like. Further examples of such deleterious oxidative changes are the loss of activity of preparations of vitamins and hormones on storage. In the case of fatty substances, for example peroxides and free fatty acids may be formed by the oxidation process. If lecithin is present, trimethylamine will easily be formed which gives the substances a fishy taste. But the oxidation may also be of a different nature from that just mentioned. Thus, for example, in the case of fatty substances, oxidation may take place without peroxide or free fatty acids being formed or in any event without these substances being formed in any detectable amount.

It is known that certain naturally occuring e.g., fatty substances, often contain substances which to a certain extent protect the material against deterioration by oxidation. Generally they are not, however, able to prevent the materials from being subjected to undesirable alterations when it is stored for a lengthy period.

Futhermore it is known that some of the oxidation changes mentioned above may be counteracted by the addition of various so-called antioxidants in small quantities. A fatty substance may thus be prevented from turning rancid by the substance being mixed with certain poly-phenols and amino-phenols. Substances such as diphenyl-guanidine, triethenolamine, alkylene-diaryl-diamines have also been proposed.

Most of the antioxidants hitherto known have, however the drawback that they are poisonous or give the material to be stabilised a bad taste and smell.

A drawback in most of the antioxidants hitherto known is that their applicability is rather limited because they are only able to counteract certain oxidation processes and show activity only in certain substances and mixtures whereas they have no effect or at any rate a considerably decreased effect against other oxidation changes and in other substances and mixtures.

These drawbacks are in accordance with the invention remedied by incorporating in the edible or potable material comprising the organic substances liable to deterioration by oxidation, a small

amount of an easily oxidizable organic phosphate of the type obtainable by phosphonylating a fermentable carbohydrate by means of yeast enzymes in the presence of an inorganic phosphate such as phosphoric acid.

The amount of the organic phosphate incorporated is not critical and generally varies from 0.1 to 2% according to the nature of the substance to be stabilised and the effect of the stabiliser on other desired properties and a preliminary test will enable those skilled in the use of antioxidants to settle the optimum proportions.

It has been proved that such substances have a greater effect and a larger field of application than the antioxidants hitherto known, this being particularly the case where the material liable to oxidation occurs dispersed or dissolved in an aqueous phase and where the known antioxidants have no effect or at any rate a decreased effect. This aqueous phase may be concentrated by evaporation to a practically dry state.

Thus, for instance coffee extract may be mentioned in which substances which give flavour occur and these substances are soluble in the aqueous phase. If this extract is concentrated its character as a dispersion becomes more and more conspicuous, and if it is concentrated to dryness, particles of flavouring constituents are obtained enclosed in grains of the water-soluble dry matter of the extraction. These grains generally contain 1—5 per cent of moisture which to some extent becomes concentrated in the surface layer enclosing the dispersed particles. It is in this surface layer that the oxidation of the flavouring constituents has its starting point. A corresponding surface layer is found in milk powder, and in butter, which are dispersions of water-in-fat. This surface layer, the interface, is found in this case around particles of water, and it is from this phase the oxidation of the fat starts.

The easily oxidizable organic phosphates suitable for carrying out the method in accordance with the invention are those of high energy value, i.e., they have a high so-called phosphate group potential (an energy-rich phosphate bond). They are thought to give the aqueous phases of the materials to be stabilized a reducing power because they are soluble in the aqueous phase which is not always the case with the antioxidants hitherto known. Owing to this circumstance the phosphates added may easily diffuse to the interfacial area, where as already mentioned the oxidation as its starting point.

After being mixed with the antioxidants, the materials to be stabilized may, if desired, be homogenised, kneaded and concentrated by evaporation or drying dependant on the nature of the material.

The phosphates used as antioxidants in accordance with the invention include hexose-, pentose-, or triose-phosphates, sulphydryl-hexose phosphates, reductone phosphates, riboflavin phosphates.

Among the hexose phosphates should especially be mentioned fructose-1,6-diphosphate, glucose-6-phosphate, fructose-6-phosphate, glucose-1-3,4- and 5-phosphate, galactose-6-phosphate. The pentose phosphates include in particular ribose-3 and 5-phosphate, and the triose phosphates dihydroxy - acetone phosphate and glycerine-aldehyde-2 and 3-phosphate.

As an example of the production of such substances may be mentioned the production of hexose - phosphates. Calcium-hexose-diphosphate, may e.g. be produced from a solution of glucose and sodium phosphate to which is added a press-juice of bottom yeast and a small quantity of toluene. After fermentation sufficient hydrochloric acid is added to give *p*H 4. After filtration the *p*H is adjusted to 7.8, and calcium chloride is added. By heating to 80° C. calcium-hexosediphosphate is separated. A monophosphate may be prepared by dissolving the diphosphate in normal hydrochloric acid, heating, and precipitating with alcohol. By this production the fact that fructose-1,6-diphosphate accumulates during the sugar fermentation, is made use of when this is produced with yeast-press-juice, and the diphosphoric acid in part forms fructose-1-phosphoric acid and in part fructose-6-phosphoric acid. Fructose-6-phosphoric acid is especially active. It is furthermore the component present during the hydrolysis of the fructose-1,6-diphosphoric acid which is most difficult to hydrolyze. This is made use of in the production of fructose-6-phosphoric acid.

By the said introduction of phosphate groups in hexoses by fermentation, phosphates of high activity are obtainable. The phosphate is transferred to the hexose by means of an enzyme, conveniently in the presence of magnesium ions. It is transferred from a phosphate donator, which in turn has the phosphate transferred from phosphate containing compounds, e.g. sodium pyrophosphate.

Instead of incorporating the organic phosphates as such to the material to be stabilised, the organic phosphate may be formed *in situ* by incorporating a mixture of substances which are able to

form the organic phosphate, e.g., small quantities of yeast press juice, an inorganic phosphate and a carbohydrate. The carbohydrate may conveniently be a hexose such as a mono-saccharide and the inorganic phosphate may conveniently be a salt such as a sodium salt of pyrophosphoric acid.

The effect of the anti-oxidant used in accordance with the invention may be increased by the addition of dicarboxylic acids, magnesium compounds, or amino acids.

If desired the antioxidants in accordance with the invention may be used in combination with known antioxidants, e.g., tocopherol.

When choosing the antioxidants to be added to the material to be stabilized care must be taken that an alkali-sensitive antioxidant is not added to an alkaline emulsion, and likewise there must not be added an acid-sensitive antioxidant to an acid emulsion.

The invention includes also the edible and potable materials containing oxidizable constituents when stabilized by the addition of one or more of the antioxidants in accordance with the invention, and also such materials as have after this addition been subjected to homogenization, kneading concentration by evaporation, drying, or the like.

The invention is further illustrated in the following examples.

EXAMPLE 1.

Hexose-phosphoric acid is added to an extract of coffee in a quantity of 1 per cent of the dry matter contained therein, after which the extract is sprayed into a current of hot air. Hereby a brown powder is obtained which is easily soluble in water. The liquid formed by the solution of the powder has the flavour of the original coffee extract, even if the powder has been stored for some time.

EXAMPLE 2.

To a cream containing about 14 per cent fat is added fructose-6-phosphate in quantity of 0.2 per cent by weight of the cream, after which the cream is homogenized. Thereby the surface of the fatty phase increases, i.e., the interface is increased. The cream thus treated is sprayed into hot air, after which a cream powder is formed which is easily soluble in water. If this powder is stored at 35°C. no oxidation of it will take place. The taste of the powder is unaltered even after a 6 months storage at 35°C, at which temperature ordinary cream powder becomes rancid and tallowy in taste in about a month.

EXAMPLE 3.

Margarine or butter is kneaded with a press juice of bottom yeast in which glucose, sodium pyrophosphate and magnesium chloride are dissolved. Such addition increases the resistibility of the substance to oxidation.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:—

1. A process of stabilizing against oxidation edible and potable materials containing organic constituents which are liable to deteriorations by oxidation, said process consisting in incorporating in the material a small quantity of an easily oxidizable organic phosphate of the type obtainable by phosphorylating a fermentable carbohydrate by means of yeast enzymes and in the presence of an inorganic phosphate such as phosphoric acid.

2. A modification of the process claimed in claim 1, in which the organic phosphate is formed *in situ* by adding ingredients capable of forming said phosphate e.g., small quantities of yeast press juice, an inorganic phosphate, and a fermentable carbohydrate to the material to be stabilized.

3. A process as claimed in claim 1 or 2 in which the carbohydrate is a hexose.

4. The process of stabilizing against oxidation edible and potable materials containing organic constituents liable to deterioration by oxidation substantially as herein described.

5. Edible and potable materials containing organic constituents liable to deterioration by oxidation when stabilized by the process claimed in any of the preceding claims.

Dated this 3rd day of January, 1946.

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